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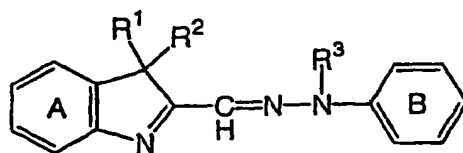
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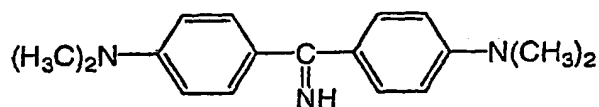
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81925 München (DE)(54) **Hair dye composition**

(57) Provided is a hair dye composition containing a direct dye (1) or (2). The hair dye composition has markedly high hair dyeing power, has less color fade over time and undergoes a smaller change in the color tone of the dye after storage.



(1)



(2)

[R<sup>1</sup>, R<sup>2</sup> and R<sup>3</sup> are the same or different and each independently represents a C<sub>1-3</sub> alkyl group and benzene ring A or B may contain a nondissociative substituent].

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## Description

## Technical Field

[0001] The present invention relates to a hair dye composition which has markedly high hair dyeing power, can impart the hair with a vivid and deep color shade ranging from greenish yellow to reddish yellow, has less color fade over time and undergoes a smaller change in the color tone of the dye even after storage.

## Background Art

[0002] Hair dyes can be classified by the dye to be used therefor, or whether they have bleaching action of melanin or not. Typical examples include a two-part permanent hair dye composed of a first part containing an alkali agent, an oxidation dye and a direct dye such as nitro dye and a second part containing an oxidizing agent; and one-part semi-permanent hair dye containing an organic acid or an alkali agent, and a direct dye such as acid dye, basic dye or nitro dye.

[0003] The above-described permanent hair dye is however accompanied with the drawbacks that color tone imparted by an oxidation dye is not so vivid and the color of the hair dyed with a vivid-color producing nitro dye ordinarily employed as a direct dye markedly fades over time and becomes dull soon even if the color tone rightly after dyeing is very vivid (Japanese Patent Application Laid-Open (*Kokai*) No. Hei 6-271435).

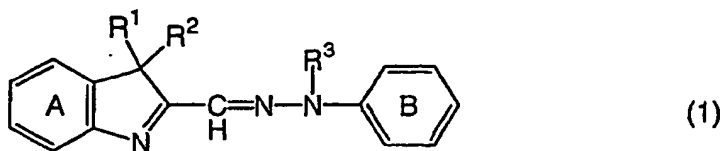
[0004] Recently, hair dyes containing as a direct dye a so-called cationic dye having a cation group contained in their conjugate system have been reported (Japanese Language Laid-Open Publication (PCT) No. Hei 8-507545, 8-501322 or 10-502946, or Japanese Patent Application Laid-Open (*Kokai*) No. Hei 10-194942). They have been found to involve drawbacks that intended dyeing effects are not available owing to decomposition of them caused by mixing, upon hair dyeing, with hydrogen peroxide ordinarily employed as an oxidizing agent; and that when the cation group is incorporated in an azo(-N=N)-based conjugated system, they are unstable to an alkali agent or a reducing agent essentially contained in a permanent hair dye.

## Disclosure of the Invention

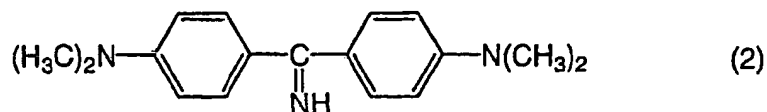
[0005] An object of the present invention is to provide a hair dye composition which features high hair dyeing power, less color fade over time and excellent storage stability permitting only a smaller color tone change of the dye after storage.

[0006] The present inventors have found that when the below-described compound which is known (in Japanese Patent Application Laid-Open (*Kokai*) No. Sho 53-8619) as a disperse dye for dry transfer printing of acidic modified synthetic fibers or as C.I. Basic Yellow 2 is used as a hair dye, the resulting dye composition can impart the hair with a vivid and deep color shade ranging from greenish yellow to reddish yellow without decomposing the dye upon hair dyeing, exhibits excellent light resistance, washing resistance, perspiration resistance, friction resistance and weather resistance, and undergoes a smaller change in the color tone of the dye after storage as compared with that rightly after preparation, because it exists stably in the composition.

[0007] In one aspect of the present invention, there is thus provided a hair dye composition comprising, as a direct dye, an azamethine compound represented by the following formula (1):



[wherein, R<sup>1</sup>, R<sup>2</sup> and R<sup>3</sup> are the same or different and each independently represents a C<sub>1-3</sub> alkyl group and benzene ring A or B may contain a nondissociative substituent; or the following formula (2):



10 [0008] In another aspect of the present invention, there is also provided a method for dyeing the hair with the above-described hair dye composition.

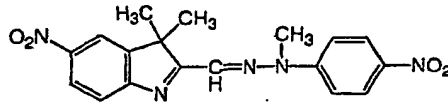
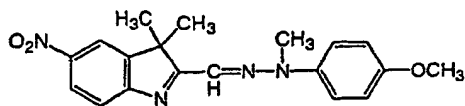
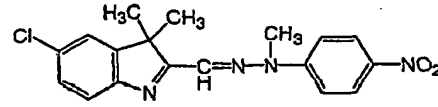
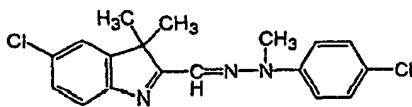
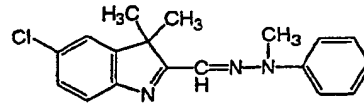
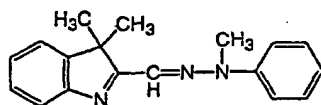
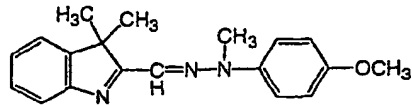
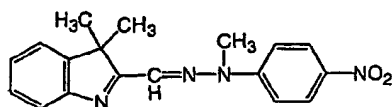
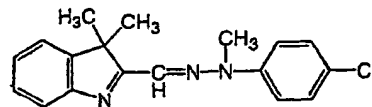
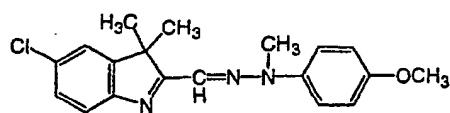
### Best Mode for Carrying out the Invention

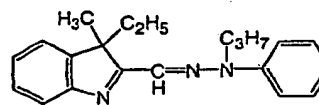
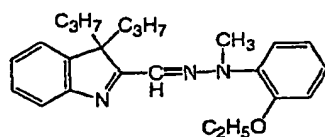
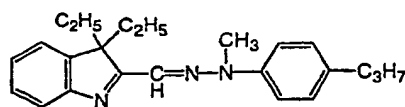
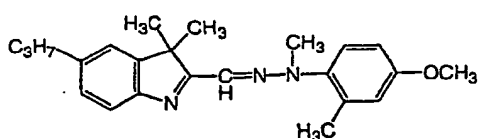
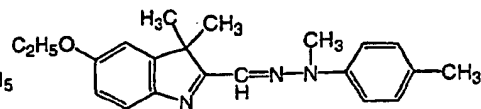
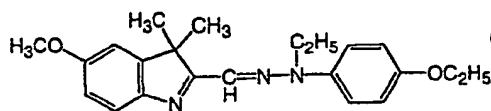
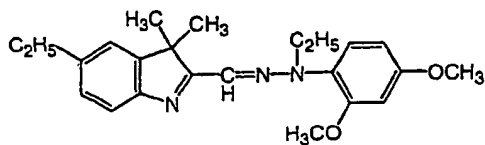
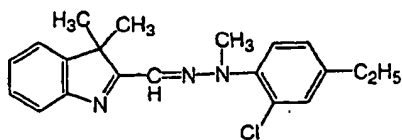
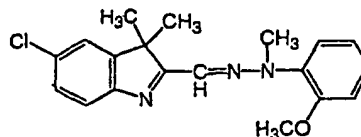
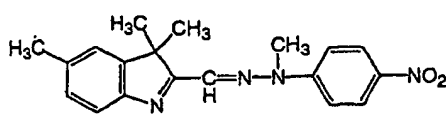
15 [0009] Compound (1) is known in Japanese Patent Application Laid-Open (Kokai) No. Sho 53-8619 as a diperse dye for dry transfer printing of acidic modified fibers, while Compound (2) is known as C.I. Basic Yellow 2. By the use of this Compound (1) or (2) as a direct dye for a hair dye composition, the hair can be imparted with a vivid and deep color shade ranging from greenish yellow to reddish yellow.

[0010] In the formula (1), examples of the C<sub>1-3</sub> alkyl group represented by R<sup>1</sup>, R<sup>2</sup> or R<sup>3</sup> include methyl, ethyl and propyl groups.

20 [0011] In the formula (1), examples of the nondissociative substituent which may be possessed by benzene ring A or B include methyl group, ethyl group, propyl group, methoxy group, ethoxy group, chlorine atom and nitro group.

[0012] Specific examples of the direct dye (1) to be used in the present invention include the following compounds:





[0013] As the direct dye (1) or (2), one or more of them may be used. Alternatively, another direct dye can be used in combination. In particular, combination with a red or blue dye makes it possible to dye the hair with a deep and highly lustrous dark brown or black color.

[0014] Examples of the direct dye other than the direct dyes (1) and (2) include Basic Blue 7 (C.I. 42595), Basic Blue 26 (C.I. 44045), Basic Blue 99 (C.I. 56059), Basic Violet 10 (C.I. 45170), Basic Violet 14 (C.I. 42515), Basic Brown 16 (C.I. 12250), Basic Brown 17 (C.I. 12251), Basic Red 2 (C.I. 50240), Basic Red 22 (C.I. 11055), Basic Red 76 (C.I. 12245), Basic Red 118 (C.I. 12251:1) and Basic Yellow 57 (C.I. 12719); and basic dyes as described in Japanese Patent Publication No. Sho 58-2204, Japanese Patent Application Laid-Open No. Hei 9-118832, Japanese Language Laid-Open Publication (PCT) No. Hei 8-501322 or Japanese Language Laid-Open Publication (PCT) No. Hei 8-507545.

[0015] The direct dye (1) or (2) is preferably added in an amount of 0.01 to 20 wt.%, more preferably 0.05 to 10 wt.%, especially 0.1 to 5 wt.% on the basis of the entirety of the composition (after mixing of all the parts when a two-part or three-part composition is employed; this will apply equally hereinafter). When another direct dye is used in combination, the content of it with the direct dye (1) or (2) preferably ranges from 0.05 to 10 wt.%, especially 0.1 to 5 wt.% based on the whole composition.

[0016] The hair dye composition of the present invention is preferably adjusted to pH 6 to 11, with pH 8 to 11 being more preferred. Examples of the alkali agent to be used for pH adjustment includes ordinarily employed ones such as ammonia, organic amines and salts thereof. The alkali agent is preferably added in an amount of 0.01 to 20 wt.%, more preferably 0.1 to 10 wt.%, especially 0.5 to 5 wt.%.

[0017] In the hair dye composition of the present invention, an oxidizing agent can be incorporated. In this case, hair

dyeing and bleaching can be carried out simultaneously, which facilitates more vivid hair dyeing. Ordinarily employed oxidizing agents, for example, hydrogen peroxide, persulfates such as ammonium persulfate, potassium persulfate and sodium persulfate, perborates such as sodium perborate, percarbonates such as sodium percarbonate and bromates such as sodium bromate and potassium bromate are usable. Out of them, hydrogen peroxide is especially preferred. The oxidizing agent is added in an amount of 0.5 to 10 wt.%, especially 1 to 8 wt.%, on the basis of the entirety of the composition.

[0018] In the hair dye composition of the present invention, an oxidation dye can be incorporated further. This incorporation enables markedly vivid dyeing not attainable by the single use of an oxidation dye. As the oxidizing agent, the above-exemplified oxidizing agents can be used, with hydrogen peroxide being particularly preferred. Alternatively, an oxidizing enzyme such as laccase can be employed. For the oxidation dye, known developers and couplers ordinarily employed for an oxidation type hair dye can be used.

[0019] Examples of the developer include p-phenylenediamines having one or several groups selected from  $\text{NH}_2$ -,  $\text{NHR}$ - and  $\text{NR}_2$ -groups (R represents a  $\text{C}_{1-4}$  alkyl or hydroxyalkyl group) such as p-phenylenediamine, p-toluylenediamine, N-methyl-p-phenylenediamine, chloro-p-phenylenediamine, 2-(2'-hydroxyethylamino)-5-aminotoluene, N,N-bis-(2-hydroxyethyl)-p-phenylenediamine, 2-hydroxyethyl-p-phenylenediamine, 2,6-dimethyl-p-phenylenediamine, methoxy-p-phenylenediamine, 2,6-dichloro-p-phenylenediamine, 2-chloro-6-methyl-p-phenylenediamine, 6-methoxy-3-methyl-p-phenylenediamine, 2,5-diaminoanisole, N-(2-hydroxypropyl)-p-phenylenediamine and N-2-methoxyethyl-p-phenylenediamine; 2,5-diaminopyridine derivatives and 4,5-diaminopyrazole derivatives; p-aminophenols such as p-aminophenol, 2-methyl-4-aminophenol, N-methyl-p-aminophenol, 3-methyl-4-aminophenol, 2,6-dimethyl-4-aminophenol, 3,5-dimethyl-4-aminophenol, 2,3-dimethyl-4-aminophenol and 2,5-dimethyl-4-aminophenol; o-aminophenols, o-phenylenediamines, 4,4'-diaminophenylamine and hydroxypropylbis(N-hydroxyethyl-p-phenylenediamine); and salts thereof.

[0020] Examples of the coupler include 1-naphthol, 1,5-dihydroxynaphthalene, 1,7-dihydroxynaphthalene, 2,7-dihydroxynaphthalene, 5-amino-2-methylphenol, 5-(2'-hydroxyethylamino)-2-methylphenol, 2,4-diaminoanisole, m-toluylenediamine, resorcin, m-phenylenediamine, m-aminophenol, 4-chlororesorcin, 2-methylresorcin, 2,4-diaminophenoxyethanol, 2,6-diaminopyridine, 2-amino-3-hydroxypyridine, 4-hydroxyindole, 6-hydroxyindole, 2,4-diamino-6-hydroxypyrimidine, 2,4,6-triaminopyrimidine, 2-amino-4,6-dihydroxypyrimidine, 4-amino-2,6-dihydroxypyrimidine, 4,6-diamino-2-hydroxypyrimidine and 1,3-bis(2,4-diaminophenoxy)propane; and salts thereof.

[0021] As a developer or coupler, at least one of the above-exemplified ones can be used. Although no particular limitation is imposed on its content, it is added in an amount of 0.01 to 20 wt.%, especially 0.5 to 10 wt.% based on the whole composition.

[0022] To the hair dye composition of the present invention, a known autooxidation dye typified by an indole or an indoline, or a known direct dye such as a nitro dye or a disperse dye can also be added.

[0023] Addition of a polyol, polyol alkyl ether, cationic or amphoteric polymer or silicone to the hair dye composition of the present invention is preferred, because the resulting hair dye composition can dye the hair uniformly and has improved cosmetic effects.

[0024] In addition to the above-described components, those ordinarily employed as a raw material for cosmetics can be added to the hair dye composition of the present invention, within an extent not impairing the advantages of the present invention. Examples of such an optional component include hydrocarbons, animal or vegetable fats and oils, higher fatty acids, organic solvents, penetration promoters, cationic surfactants, natural or synthetic polymers, higher alcohols, ethers, amphoteric surfactants, nonionic surfactants, protein derivatives, amino acids, antiseptics, chelating agents, stabilizing agents, antioxidants, plant extracts, crude drug extracts, vitamins, colorants, perfumes and ultraviolet absorbers.

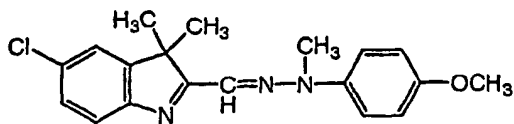
[0025] The hair dye composition of the present invention can be prepared in a conventional manner into a one-part composition, a two-part composition having a first-part component containing an alkali agent and a second-part component containing an oxidizing agent, or a third-part composition having, in addition to these two components, a powdery oxidizing agent such as persulfate. The direct dye (1) or (2) can be incorporated in either one or both of these components of the two-part or three-part composition. The one-part type is applied to the hair directly, while the two- or three-part type is applied to the hair after mixing these parts upon hair dyeing.

[0026] No particular limitation is imposed on the form of the hair dye composition of the present invention. Examples include powder, transparent liquid, emulsion, cream, gel, paste, aerosol, and aerosol foam. It preferably has a viscosity of 2000 to 100000 mPa·s in the stage of application to the hair (after mixing of all the parts when a two-part or three-part type composition is employed).

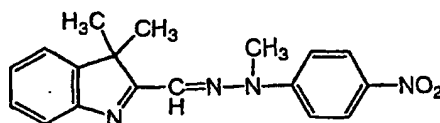
-Examples-

[0027] Compounds employed in the below-described examples are as follows:

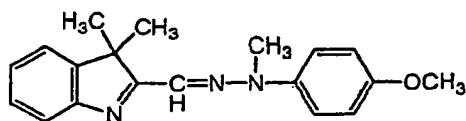
Compound (a)



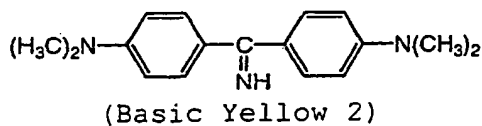
Compound (b)



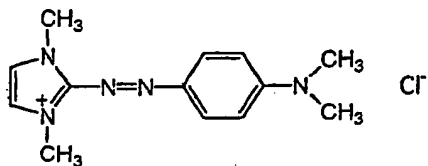
Compound (c)



Compound (d)



Compound (e)



## Examples 1 to 5

[0028] In a manner known per se in the art, hair dyes as shown in Table 1 were prepared.

[0029] The data appearing in each of the following tables represent "wt.%".

Table 1

		Examples				
		1	2	3	4	5
5	Dye [Compound (a)]	0.2		0.15	0.1	
	Dye [Compound (d)]		0.5		0.1	0.2
	Dye [Compound (e)]			0.15	0.1	0.05
10	Dye [Basic Blue 26]			0.1	0.1	
	Ethanol		5		5	5
	Propylene glycol			5		5
15	Diethylene glycol monoethyl ether		10			
	Guar gum	1				
	Hydroxypropyl guar gum		1	1	1	1
	"Gufquat 734" (trade name; product of ISP Japan)	1		1		
20	"Catinal LC100" (trade name; product of Toho Chemical Industry)		1			1
	"Polyether-modified silicone KF6005" (trade name; product of Shin-Etsu Chemical)					0.4
25	"Amodimethicone SM8702C" (trade name; product of Dow Corning Toray Silicone)				1.5	
	Monoethanolamine	0.1				
	Phosphoric acid	Amount to adjust pH to 9				
30	Perfume	q.s.				
	Water	Balance				
	Total (g)	100				

35 Examples 6 to 9

[0030] In a manner known per se in the art, hair dyes as shown in Table 2 were prepared.

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Table 2

		Examples			
		6	7	8	9
1st part	Dye [Compound (b)]	0.2		0.15	0.2
	Dye [Compound (d)]		0.1	0.15	
	Dye [Compound (e)]		0.2		0.05
	Dye [Basic Blue 99]		0.3		
	28 wt.% aqueous ammonia	5			
	Monoethanolamine	2			
	Propylene glycol	8			
	Polyoxyethylene (20) isostearyl ether	24			
	Polyoxyethylene (2) isostearyl ether	20			
	"Merquat 280" (trade name; product of Calgon Corp., a 35 wt.% aqueous solution)	8			
	"Polymer JR400" (trade name; product of Union Carbide)		0.5		0.5
	"Amodimethicone SM8702C" (trade name; product of Dow Corning Toray Silicone)			2	
	"Polyether modified silicone KF6005" (trade name; product of Shin-Etsu Chemical)				0.3
	Tetrasodium ethylenediaminetetraacetate	0.1			
	Perfume	q.s.			
	Ammonium chloride	Amount to adjust pH to 10			
	Water	Balance			
2nd part	35 wt.% aqueous hydrogen peroxide	17.1			
	Methylparaben	0.1			
	Phosphoric acid	Amount to adjust pH to 3.5			
	Water	Balance			

Examples 10 to 12

[0031] In a manner known per se in the art, hair dyes as shown in Table 3 were prepared.



Table 3

			Examples		
			10	11	12
5	1st part	Toluene-2,5-diamine	1.9	1	
		Para-aminophenol			1
		Resorcin	2		
10		Para-amino-ortho-cresol			1.1
		2,4-Diaminophenoxyethanol		1.37	
		Dye [Compound (b)]	0.05		
15		Dye [Compound (d)]		0.15	
		Dye [Compound (c)]			0.1
		28 wt.% aqueous ammonia	5		
		Monoethanolamine	2		
20		Propylene glycol	8		
		Polyoxyethylene (20) isostearyl ether	24		
		Polyoxyethylene (2) isostearyl ether	20		
25		"Merquat 280" (trade name; product of Calgon Corp., a 35 wt.% aqueous solution)	8		
		"Polymer JR400" (product of Union Carbide)		0.5	
30		"Amodimethicone SM8702C" (trade name; product of Dow Coming Toray Silicone)			2
		Sodium sulfite	0.05		
		Ascorbic acid	0.5		
		Tetrasodium ethylenediaminetetraacetate	0.1		
35		Perfume	q.s.		
		Ammonium chloride	Amount to adjust pH to 10		
		Water	Balance		
40	2nd part	35 wt.% Aqueous hydrogen peroxide	17.1		
		Methylparaben	0.1		
		Phosphoric acid	Amount to adjust pH to 3.5		
45		Water	Balance		

## Example 13

[0032] In a manner known per se in the art, the following hair dye was prepared.

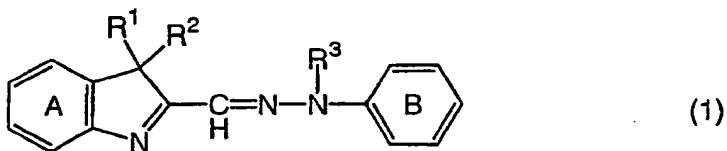
(First part)	(wt.%)
Para-aminophenol	1
Para-amino-ortho-cresol	1.1
Compound (d)	0.1
28 wt.% aqueous ammonia	5
Monoethanolamine	2
Cetanol	8.5

(continued)

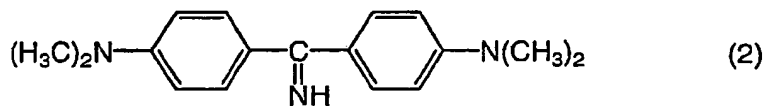
(First part)	(wt.%)
Polyoxyethylene (40) cetyl ether	3
Polyoxyethylene (2) cetyl ether	3.5
Stearyl trimethyl ammonium chloride	2
Liquid paraffin	0.5
Sodium sulfite	0.05
Ascorbic acid	0.5
Tetrasodium ethylenediaminetetraacetate	0.1
Perfume	q.s.
Ammonium chloride	Amount to adjust pH to 10
Water	Balance
(Second part)	(wt.%)
35 wt.% Aqueous hydrogen peroxide	17.1
Methyl paraben	0.1
Phosphoric acid	Amount to adjust pH to 3.5
Water	Balance

## Claims

1. A hair dye composition comprising, as a direct dye, an azamethine compound represented by the following formula (1):



(wherein, R<sup>1</sup>, R<sup>2</sup> and R<sup>3</sup> are the same or different and each independently represents a C<sub>1-3</sub> alkyl group and benzene ring A or B may have a nondissociative group; or the following formula (2) :



2. A hair dye composition according to claim 1, further comprising an oxidizing agent.
3. A hair dye composition according to claim 1 or 2, further comprising an oxidation dye.
4. A method for dyeing the hair with a hair dye composition as claimed in any one of claims 1 to 3.

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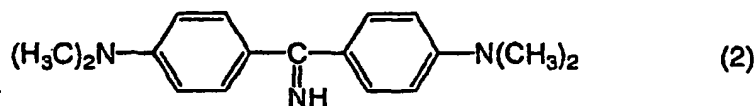
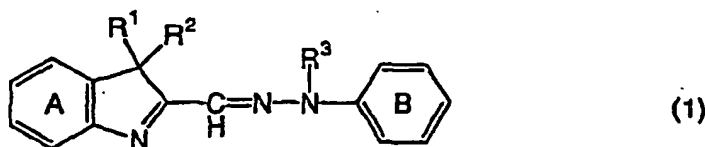
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(54) **Hair dye composition**

(57) Provided is a hair dye composition containing a direct dye (1) or (2). The hair dye composition has markedly high hair dyeing power, has less color fade over time and undergoes a smaller change in the color tone of the dye after storage.



[R<sup>1</sup>, R<sup>2</sup> and R<sup>3</sup> are the same or different and each independently represents a C<sub>1-3</sub> alkyl group and benzene ring A or B may contain a nondissociative substituent].

**EP 1 133 977 A3**



European Patent  
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# EUROPEAN SEARCH REPORT

Application Number  
EP 01 10 6328

DOCUMENTS CONSIDERED TO BE RELEVANT			
Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int.Cl.7)
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			TECHNICAL FIELDS SEARCHED (Int.Cl.7)
			A61K
<del>The present search report has been drawn up for all claims</del>			
Place of search		Date of completion of the search	Examiner
Berlin		15 September 2003	Krische, D
CATEGORY OF CITED DOCUMENTS X : particularly relevant if taken alone Y : particularly relevant if combined with another document of the same category A : technological background O : non-written disclosure P : intermediate document T : theory or principle underlying the invention E : earlier patent document, but published on, or after the filing date D : document cited in the application L : document cited for other reasons & : member of the same patent family, corresponding document			

EPO FORM 1503 03.82 [P04C01]



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#### CLAIMS INCURRING FEES

The present European patent application comprised at the time of filing more than ten claims.

- ☐ Only part of the claims have been paid within the prescribed time limit. The present European search report has been drawn up for the first ten claims and for those claims for which claims fees have been paid, namely claim(s):
- ☐ No claims fees have been paid within the prescribed time limit. The present European search report has been drawn up for the first ten claims.

#### LACK OF UNITY OF INVENTION

The Search Division considers that the present European patent application does not comply with the requirements of unity of invention and relates to several inventions or groups of inventions, namely:

see sheet B

- ☐ All further search fees have been paid within the fixed time limit. The present European search report has been drawn up for all claims.
- ☐ As all searchable claims could be searched without effort justifying an additional fee, the Search Division did not invite payment of any additional fee.
- ☐ Only part of the further search fees have been paid within the fixed time limit. The present European search report has been drawn up for those parts of the European patent application which relate to the inventions in respect of which search fees have been paid, namely claims:
- ☒ None of the further search fees have been paid within the fixed time limit. The present European search report has been drawn up for those parts of the European patent application which relate to the invention first mentioned in the claims, namely claims:

1-4 in part



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LACK OF UNITY OF INVENTION  
SHEET B

Application Number  
EP 01 10 6328

The Search Division considers that the present European patent application does not comply with the requirements of unity of invention and relates to several inventions or groups of inventions, namely:

1. claims: 1-4 in part

Hair dye composition comprising an azamethine compound of  
formula (1) and method using this composition  
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2. claims: 1-4 in part

Hair dye composition comprising an azamethine compound of  
formula (2) and method using this composition  
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**ANNEX TO THE EUROPEAN SEARCH REPORT  
ON EUROPEAN PATENT APPLICATION NO.**

EP 01 10 6328

This annex lists the patent family members relating to the patent documents cited in the above-mentioned European search report.  
The members are as contained in the European Patent Office EDP file on  
The European Patent Office is in no way liable for these particulars which are merely given for the purpose of information.

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For more details about this annex : see Official Journal of the European Patent Office, No. 12/82